Smart Paint for anodic protection of steel

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Abstract

In order to overcome the difficulties associated to the solubility and mechanical integrity of polyaniline (PAni) films, in this work we develop a binder by mixing PAni in the oxidized and undoped state (emeraldine base form) with 4-chloro-3-methylphenol, a plasticizer, and solvent. This binder has been used as a coating alone or combined with a conventional nitrocellulose paint to formulate the called Smart Paint. The characterization of binder films, which are cohesive and self-standing, shows the preservation of PAni properties, indicating that they satisfy the typical characteristics of anticorrosive coatings. Electrochemical assays have been carried out in H_2SO_4 solution using AISI 1006 steel plates coated with the binder and the Smart Paint. Results indicate that the binder and the Smart Paint promote the passivation of the metal substrate, reflecting their protecting abilities against corrosion.

Keywords: Corrosion; Anodic protection; Polyaniline; Binder; Smart Paint

1. INTRODUCTION

Many metals undergo corrosion in an interval of potentials defined by the pH and the surrounding conductive electrolyte. However, the corrosion can be arrested by making more negative the potential through a current that flows onto the metal from the electrolyte (cathodic protection). Another effective technique to prevent corrosion on a metal surface is to transform it into the anode of an electrochemical cell, controlling the potential in a zone where the metal is passive (*i.e.* passivation interval for the anodic protection) [1]. In opposition to cathodic protection, anodic protection applies anodic current on the structure to be protected.

The fundamental principles of the anodic protection technique were introduced in the middle of the twentieth century, when it was applied to control the corrosion in boilers made of stainless steel exposed to sulfuric acid solutions [2,3]. Currently, anodic protection is particularly effective to prevent corrosion damages in steel tanks and pipes in contact with concentrated acid and alkaline environments. Application of this protection technique to common and relatively cheap austenitic stainless steels allows not only to reduce the economic impact of corrosion but also to preserve the environment.

Anodic protection involves raising the potential of the metal for the development of a passive thin layer at the surface, which is formed by oxides of the own metal. This oxide layer acts as a protective barrier able to isolate the surface of the substrate from the electrolyte [2,4]. In practice, anodic protection can be used to protect metals and alloys (*e.g.* iron, carbon steel, stainless steel, titanium, aluminum, chrome, and nickel) from extremely corrosive environments (*e.g.* sulfuric and phosphoric acids, and caustic soda) [5].

The corrosion in harsh environments has aroused in the scientific community the need to formulate smart coatings that stimulate upon external effects (pressure, temperature, corrosion, stress, physical contact with other materials, etc.), allowing a selective, fast and effective response to protect against corrosion of metallic materials. There are records in

literature of several initiatives in the production of smart coatings (*e.g.* as paints constituted of pigments of zeolitic rock, nanoparticles of CeO_2, Cr_2O_3 and conductive polymers). These smart coatings use the intrinsic properties of their components, which associatewith specific technologies and environments, to combat the action of corrosive processes [6-8].

Coatings based on intrinsically conducting polymers (ICP) represent a promising alternative to anodic passivation for the protection of metals, complementing or even replacing the application of external anodic currents. Due to their intrinsic properties, oxidized ICP in contact with metals undergo a reduction inducing the formation or preservation of protective oxides, as occur upon the application of an external current [9-13]. The temporal efficacy of these films in the passivation of the metals increases with the amount of ICP.

Passivation of metals using ICP is due to layers of protective oxides produced through an electron transfer mechanism (*i.e.* oxidation-reduction reactions in the metal/polymer system). Accordingly, totally or partially oxidized (charged) ICP provide protection to the metal against corrosion until they become totally uncharged (*i.e.* 100% of reduction) [12,14]. Another requirement to protect metals using this technology is based on the fact that the reduction of the ICP and the passivation of the metal must occur in the same interval of potentials. Specifically, the layer of protective oxides produced during the passivation process disappears when the reduction potential of the ICP is lower than the passivation potential of the metal [9,11 and 12]. If the reduction potential of the ICP is lower than the passivation potential of the metal in the electrolytic medium, the reduction of the polymer results in a faster corrosion process of the metal substrate. This is because the reduction of the polymer occurs below the Flade potential, where corrosion is accelerated.

Direct application of ICP in corrosion protection is frequently limited by the poor solubility and processability of these materials, which are typically employed as pigments dispersed in conventional polymeric matrices [15-19]. Passivation using such strategy

requires a concentration of ICP high enough to guarantee the physical contact between pigment particles as well as between the pigment particles and the metal surface. This condition is also required by zinc-containing coatings typically used for the cathodic protection of metals, even though in such paints the high content of zinc particles acts in detriment of the mechanical properties of the protective film.

Synthesis of ICP is usually performed using relatively simple and safe processes in aqueous solutions. Furthermore, these materials, which are obtained using relatively cheap monomers, frequently combine two interesting properties: good environmental stability and reversible oxidation-reduction processes [20].

Polyaniline (PAni) is the most extensively studied ICP, which should be attributed to its unique characteristics: chemical stability, relatively high electrical conductivity, some solubility in organic solvents, excellent environmental stability of its conducting and non-conducting forms, and, specially, the simplicity of the synthetic route used for its preparation and the low cost of the monomer (aniline) [21-25]. PAni can be found in two reduced forms (*i.e.* leucoemeraldine base and protonated leucoemeraldine) and two oxidized forms (*i.e.* the half oxidized emeraldine base and protonated emeraldine, abbreviated PAni EB and PAni EP, respectively) [13].

PAni EP (conductive) has been used in most studies of production of organic coatings as pigment (powder) dispersed in a conventional polymeric matrix. This configuration prevents the maximum physical contact among polymeric PAni chains and with both the electrolyte and the metal to be protected, representing a reduction in in the formation and maintenance of protective oxides on metallic substrates. However, self-standing films with conducting PAni using plasticizers and dopant plasticizers were successfully prepared and applied for the inhibition of electromagnetic radiation [21,26]. Unfortunately, materials with ionic or electronic conducting properties should be avoided to preserve the barrier properties of the protecting coating.

These features have motivated the present study, which is aimed to use oxidized and undoped PAni EB for the preparation of adherent anticorrosive coatings based on self-standing films with good barrier properties. For this purpose, oxidized and doped PAni EP has been transformed into PAni EB, and subsequently combined with a plasticizer, 4-chloro-3-methylphenol (CMP), and an organic solvent to produce a binder. In order to obtain organic coatings able to protect metallic substrates from corrosion using the anodic passivation mechanism, this binder was produced using two different strategies: addition of the binder to a conventional paint and direct application of the binder as a resin to form the Smart Paint.

The contribution of this study to the present knowledge about ICP-based coatings is associated to the fact that PAni is added to the paint after being mixed with a plasticizer, allowing its incorporation as a resin and not as a pigment (finely milled powder of PAni), as it is usually done [27-29]. By applying this procedure, it is expected that, inside the coating, PAni particles/molecules will be in physical contact among them and with the metallic surface. This physical contact favors the participation of the total amount of added PAni as active agent, producing the Smart Paint. On the other hand, considering that PAni is slightly soluble, when added as a pigment, solid PAni particles are encapsulated by the conventional resin hampering its role as an active agent on the Smart Paint.

Another novelty to be emphasized is the use of carbon steel as electrode instead of stainless steel or pure iron, as occur in most of the cases reported in the literature, to demonstrate the performance of organic coatings as agents of anodic protection.

2. EXPERIMENTAL

2.1. Materials

$(NH_4)_2S_2O_8$ and CMP were purchased from Aldrich, HCl from Merck, NH_4OH and aniline from Synth, and $CHCl_3$ from Vetec. The monomer was previously distilled. PAni EP was prepared in a 20 L capacity double-walled reactor, under controlled agitation and

temperature. A solution of $(NH_4)_2S_2O_8$ (0.4 mol·L^{-1}) in HCl (1.5 mol·L^{-1}) was added slowly under constant stirring at -5 °C to a second HCl solution (1.5 mol·L^{-1}) containing aniline (0.4 mol·L^{-1}). In addition to the time required for the addition of the oxidizing agent, the reaction was kept at -5ºC (± 1 ºC) and under agitation for 5h. The resulting PAni EP was filtered and subsequently added to a 0.5 mol·L^{-1} NH_4OH aqueous solution using a 1:15 (g/mol) PAni EP: solution ratio. The formed emulsion was maintained at pH = 10 and under moderate stirring for 6 h. Finally, the solid was filtered and washed with a NH_4OH solution (0.5 mol·L^{-1}) until it became colorless. PAni EB obtained from this treatment was dried in an oven at 60 ºC for 24 h [30].

2.1.1 Binder preparation

For the production of Smart Paint and PAni EB films was necessary the production a binder that allows the homogeneous solubilization of PAni EB in a plasticizer, as the CMP, with the aid of an organic solvent. The PAni EB binder was produced by mixing PAni EB, CMP and $CHCl_3$ (1:2:10 mass ratio) in a closed flask with mechanical agitation at 1500 rpm (Dispermat Model N1) for 6 h.

2.1.2 Smart Paint preparation

The preparation of the Smart Paint was performed with the incorporation of PAni EB binder to a commercial paint based on nitrocellulose (Nitrocellulose Lacquer ZynaMix AUTOCOLOR, produced by Pittsburgh Plate Glass Company Industries Brazil (PPG - Brazil)). This permits the complete incorporation of the PAni as a resin and not as a pigment.

Two different Smarts Paints, which differ in the concentration of PAni EB binder, were prepared by mixing this product (0.25% w/w and 0.50% w/w) with Nitrocellulose Lacquer ZynaMix AUTOCOLOR, produced by PPG - Brazil. The mixture was kept under agitation at 1500 rpm (Dispermat Model N1) for 2 h.

Anodic protection assays were performed by applying the binder alone (hereafter denoted "PAni EB Film") and mixed with a commercial nitrocellulose paint (hereafter referred as "Smart Paint"). AISI 1006 steel panels were used as metallic substratum for corrosion experiments. The elemental composition of this steel is: C < 0.08%, Mn > 0.25% and < 0.40%, P < 0.04% and S < 0.05%. Rectangular steel pieces of 1×25×50 mm^3 and 1×50×100 mm^3 were degreased at 45 ºC for 15 min with a commercial alkaline degreaser (Saloclean 619L – Klintex Insumos Indústrias Ltda), washed with distilled water and, subsequently, dried using an airflow.

2.2. Equipments

The PAni EB binder was applied by spin coating directly onto the steel substrate at 1000 rpm during 10 s and, subsequently, at 2500 rpm during 30 s. Spin coating was performed using a Spin Coater KW-4A. Smart Paint was applied by immersion of steel panels in a Deep-Coating MA 765-Marconi using an immersion speed and immersion time of 10 $mm \cdot s^{-1}$ and 30 s, respectively. After coating, steel panels were dried by keeping them at room temperature for 48 h. Films for spectroscopic assays were obtained using similar procedures but on glass panels, from which they were easily peeled off. The thickness of the films was determined using a Fischer Dualscope MP20 equipment and corresponds to the average of nine independent measures at different zones of each film.

Structural characterization of the coating films was performed using a Perkin Elmer Spectrum 1000 FTIR spectrometer (1% mixture of the sample in KBr) and a Dilor X-Y dispersive Raman spectrometer equipped with a 1024 diode multichannel detector and He/Ne laser with 632.8 nm of excitation (directly applied on the samples).

Cyclic voltammetry (CV), open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) assays were carried out with a potentiostat AUTOLAB PGSTAT 302 Ecochemie. Cyclic voltammograms were recorded at a scan rate of 25 $mV \cdot s^{-1}$. The initial and final potential was $-0.50 \cdot V_{Ag|AgCl}$, while the reversal potential was $+1.50 \cdot V_{Ag|AgCl}$. The amplitude of the EIS perturbation signal was 10 mV and the frequency

ranged from 10^{-5} to 10^{2} Hz. CV and OCP experiments were controlled through the GPES software while the FRA software was used for the EIS assays. All electrochemical experiments were carried out in 0.2, 2.0 and 4.0 $mol \cdot L^{-1}$ H_2SO_4 aqueous solutions. Experiments were carried out in a standard three-electrode cell. The coated AISI 1006 steel panel was used as working electrode (WE), platinum wires (99.99%) and the Analion Ag|AgCl reference electrode serving as the counter electrode (CE) and the reference electrode (RE), respectively. The RE was associated to a Luggin capillary located at 1 mm from the WE. OCP measures were monitored during 3000 s after the initial polarization, which was carried out by applying an external potential of $+1.00 \cdot V_{Ag|AgCl}$ during 5 s.

EQUIPOS DE MICROSCOPIA ????

3. RESULTS AND DISCUSSION

3.1. Morphology of PAni EB Films

The binder obtained from the mixture of CMP and PAni EB is expected to present a homogeneous mixture of the two components. Similarly, the addition of such binder to a nitrocellulose commercial paint is expected to produce a homogeneous distribution of the PAni EB in the matrix of the paint, enabling the physical contact not only among PAni EB chains but also of PAni EB molecules with the surrounding medium and with the metal to be protected.

Fulfillment of this hypothesis should result in a PAni EB network or Smart Paint, like that schematized in Figure 1, able to involve all the polymer chains in oxidation and reductions reactions to protect the AISI 1006 steel substrate against corrosion through an anodic protection mechanism.

Figure 1

Films were prepared by spreading the PAni EB binder onto glass substrates. After solvent evaporation, the detached films were found to be self-standing showing good mechanical integrity. Films, which were completely cured after 48 h, were analyzed by optical microscopy (Figure 2ab) and SEM (Figure 2cd).

As it can be seen, images and micrographs revealed a compact and homogeneous material in which there is no possibility of distinguishing between the CMP and PAni EB components. In SEM images (Figures 2cd), it can be seen that the PAni is not present in the form of a finely divided powder but in the form of a polymer with its macromolecules dispersed with the aid of the plasticizer.

Figure 2

3.2. FTIR and Raman Spectroscopy

The FTIR spectrum of PAni EB (Figure 3) shows intense absorption bands at 1580 cm^{-1} and 1493 cm^{-1}, which were associated with the $C{=}C_{Aromatic}$ stretching of the quinoid and benzenoid rings, respectively. This assignment was corroborated by the ratio of these peaks, which evidenced that the presence of quinoid and benzenoid units was similar (*i.e.* 50% of each type), as is characteristic of the emeraldine base form [10,17]. On the other hand, the FTIR spectrum recorded for the PAni EB Films (Figure 3) clearly correspond to the sum of the bands detected in the spectra of the binder's individual components (*i.e.* CMP and PAni EB).

Figure 3

The bands observed in the Raman spectrum of PAni EB (Figure 4) at 1612 and 1591 cm^{-1} were assigned to the C–C stretching of the benzenoid ring and the C=C stretching of the quinoid ring, respectively, whereas the bands at 1497 and 1470 cm^{-1} were attributed to the C=N stretching of oxidized PAni [31-35]. The reduction of PAni is typically related with conformational changes in the dihedral angles linking the quinoid and benzenoid rings, which affect the bands of the oxidized PAni at 1591 and 1167 cm^{-1} [31]. However, these alterations are not identified in Figure 4. On the other hand, protonated PAni typically shows a band related with the $C–N^{+}$ stretching, which appears in the 1300-1350 cm^{-1} region of the Raman spectrum [31,33]. As it was expected, the Raman spectrum displayed in Figure 4 for the PAni EB Film corresponds to the sum of the PAni EB and CMP spectra.

The overall of the results corroborate that the PAni produced in this work corresponds to the emeraldine base, remaining in such oxidized non-conducting state when it is incorporated to the PAni EB Film. Thus, CMP does not act as a reducing and/or protonic

agent for PAni EB, which is consistent with its role as protecting agent able to promote the anodic protection effect in passivized metals associated to a barrier effect.

Figure 4

3.3. Electrochemical characterization

Figure 5 displays the control voltammogram in the -0.50 - +1.50·$V_{Ag|AgCl}$ interval of an AISI 1006 steel electrode immersed in 0.2 mol·L^{-1} H_2SO_4. The presence of anodic current evidences that the electrode is active until a potential of +0.33 $V_{Ag|AgCl}$ is reached. The latter value corresponds to the Flade potential, showing a sharp drop of the current to values near zero. This phenomenon, which remains until +1.50·$V_{Ag|AgCl}$, is due to the formation of a layer of stable and passivating oxides on the surface. Inspection of the reverse scanning indicates that the layer of oxides is destroyed at +0.32·$V_{Ag|AgCl}$, which is evidenced by a sudden increase of the current, the electrode remaining active until the end of the experiment. As shows Figure 5, the steel is passivated in this medium for potentials greater than +0.32 $V_{Ag|AgCl}$, allowing the performance of a Smart Paint to the maintenance of oxide layer passivating formed in this electrolyte and under these conditions.

Control voltammograms recorded for AISI 1006 steel panels covered by PAni Film (average thickness of the coating: 33±16 μm) showed a different behavior. The representative voltammogram, which is included in Figure 5, shows the oxidation and reduction potentials at +0.25·$V_{Ag|AgCl}$ and +0.75·$V_{Ag|AgCl}$, respectively, as is typically observed for PAni EB [9,12 and 17]. Thus, the redox pair of PAni EB Film appears within the region of potentials able to passivate the AISI 1006 steel, corroborating that such coating induces a change in the electrochemical behavior of the electrode.

Figure 5

3.4. Corrosion monitoring

The action of the Smart Paint in the induction or maintenance of corrosion protection can be shown by determining the OCP and its variation over time. In the case of the OCP measured for the metal/Smart Paint system, if the potential is maintained over time in the potentials region in which the metal if passive, without application of external current, is being demonstrating the effective action of Smart Paint in the protection anodic.

Figure 6 displays the OCP measured for AISI 1006 steel electrodes coated with PAni EB Film immersed in 0.2, 2.0 and 4.0 $mol \cdot L^{-1}$ H_2SO_4 solutions after 5 s of polarization at $+1.00 \cdot V_{Ag|AgCl}$. As it can be seen, the potential remains constant at $+0.45 \cdot V_{Ag|AgCl}$ during 580, 470 and 370 s, respectively, the metallic substrate being passivized at such values as was shown above (Figure 5). After such time, the potential drops instantaneously to $-0.40 \cdot V_{Ag|AgCl}$, which is the characteristic corrosion potential of the substrate in the corrosive environment considered in this work. On the other hand, the potential drops to $-0.40 \cdot V_{Ag|AgCl}$ at the beginning of the experiment when a bare steel electrode is considered (Figure 6).

Despite the short time of action as anodic protection, it is shown that the PAni EB film protects the carbon steel dipped in 0.2, 2.0 and 4.0 $mol.l^{-1}$ H_2SO_4 solutions through formation and/or maintenance the protection oxides layer. The short time of protection obtained can be attributed to low action of barrier effect produced by this thin film, which requires of PAni an active role in maintaining the integrity of the passivating oxide layer on a large area of the electrode.

Figure 6

Figure 7 compares the OCP determined for electrodes coated with Smarts Paints, which were fabricated by mixing Nitrocellulose Lacquer ZynaMix AUTOCOLOR paint and

different concentrations of the PAni EB binder (0.25% and 0.50% w/w), with that measured for an electrode coated with the unmodified commercial paint. Experiments were performed using the experimental conditions previously applied for electrodes coated with PAni EB Films. The electrode coated with the unmodified nitrocellulose paint drops instantaneously from $+1.00 \cdot V_{Ag|AgCl}$ to $-0.45 \cdot V_{Ag|AgCl}$, the latter value being consistent with the corrosion potential of the metallic substrate in the investigated environment. For the electrodes coated with the 0.25% and 0.50% w/w binder-containing Smart Paint, the potential drops to $+0.45 \cdot V_{Ag|AgCl}$, remaining at such value during 1500 and 2300 s, respectively. After this period, the potential decreases to approximately $-0.45 \cdot V_{Ag|AgCl}$.

It is worth noting that PAni EB Film and Smart Paint coatings show an interval of time in which the potential of the coated carbon steel electrode is compatible with the formation and preservation of a passivating oxide layer. The existence of this layer is due to the presence of the ICP in the binder used to prepare the binder and the modified paints.

Results indicate that the passivating oxide layer is preserved during a smaller period of time when the binder is directly applied as PAni EB Film than when it is used as additive to modify a conventional commercial paint. This is a striking feature since the concentration of the ICP is around 100-200 times higher in the PAni EB Film than in the modified Smarts Paints (*i.e*. the thickness of the coating has been considered in this estimation). The behavior of the Smarts Paints should be related not only with the concentration of the ICP but also with the barrier effect induced by the own nitrocellulose coating. Thus, PAni EB Film does not offer protection through the barrier effect, passivation of the electrode surface being exclusively due to the reduction of PAni. In contrast, electrodes coated with Smarts Paints are essentially protected by the barrier effect induced by the nitrocellulose paint, the ICP acting in the structural defects of the coating only. This protection mechanism is fully consistent with the fact that the protection imparted by Smarts Paints grows with the concentration of binder

added to the nitrocellulose paint (*i.e.* the protection imparted by the Paint with a binder concentration of 0.50% w/w is higher than that containing 0.25% w/w).

Representation of the OCP measures against time indicates that PAni EB is able to passivate AISI 1006 steel panels immersed in a corrosive H_2SO_4 aqueous solution, protecting this substrate during a period of time that depends on both the area of the electrode and the concentration of PAni EB in the coating. Moreover, it should be mentioned that, in opposition to the suggestions reported by different authors, no spontaneous re-oxidation of the ICP was observed [36-38].

Figure 8 displays the Nyquist plots obtained for both bare and coated steel panels in 0.2 $mol \cdot L^{-1}$ H_2SO_4. Immersion of the bare AISI 1006 steel electrode in the H_2SO_4 solution during 300 s results in a semicircle (Figure 8a), the resistance determined at the end of the experiment from the intercept of such semicircle with the real axis (Z') at the end of the experiment being of ~50 $\Omega \cdot cm^2$. This spectrum is similar to that typically observed for carbon steel electrodes in H_2SO_4 with an already installed corrosion process [39]. The spectrum of the electrode coated by PAni EB Film (Figure 8b) shows a completely different behavior after 300 s of immersion in 0.2 $mol \cdot L^{-1}$ H_2SO_4, which is consistent with the observations displayed in Figure 6. Thus, the Nyquist plot is characterized by different regions: a semicircle in the high frequency region, a zone with a maximum inclination of 45º at intermediate frequencies, and a nearly vertical straight line in the low frequency region.

The semicircle at high frequencies indicates the presence of a charge transfer process at the interface between the coating and the electrodes, which corresponds to the reduction of the polymer and the oxidation of the metal for the formation of the passivating oxide layer. The charge transfer resistance, which is determined by the diameter of semicircle, is lower for the steel electrode coated with the PAni EB Film than for the bare electrode. This should be attributed to the fact that the charge transfer process is slower at the electrolyte/metal interface than at the PAni EB Film/metal interface [40-43].

The region at intermediate frequencies, which show a line with a slope of around 45º, has been attributed to the ionic diffusion associated to the transport of dopant ions (HSO_4^-) from the solution to the polymeric matrix. This corresponds to the Warburg impedance behavior, which explains the doping of the PAni EB. Finally, the nearly vertical line at the low frequency range evidences the importance of the capacitive impedance response. This has been related with the film thickness, the limited amount of polymer able to participate in the oxidation-reduction processes, and the interruption of the diffusion at one end of the film/electrode system [40,44]. These features suggest the existence of ferric oxides (passivation) at the metal surface, which enhance the electric resistance provoking the anodic protection of the metallic substrate.

EIS results obtained for the bare and coated electrodes after 900 s of immersion in a 0.2 $mol \cdot L^{-1}$ H_2SO_4 solution are displayed in Figure 8b. This period of time exceeds the protecting ability imparted by the PAni EB Film, the two electrodes being in the corrosion potential of AISI 1006 steel at this corrosive medium. The diameters of the semicircles observed for the bare electrode and the electrode coated with PAni EB Film correspond to resistances of 8 and 11 $\Omega \cdot cm^2$ (including the electrolyte resistance), respectively. Thus, once the anodic protection period has been exhausted, the EIS behavior of the coated electrode is practically identical to that of the bare electrode.

Figure 8

4. CONCLUSIONS

Formulation of the binder has been used to produce *free standing* PAni EB Films, in which the PAni remains dedoped and oxidized after the curing process. The latter is essential to avoid the formation of films with ionic or electronic conductivity and, therefore, able to protect the metals against the corrosion by anodic protection.

CV assays allowed us to identify the formation of redox pairs characteristic of PAni EB in the potential interval corresponding to the passivation of AISI 1006 steel. Moreover, OCP *vs.* time measurements on panels coated with PAni EB Films immersed in a H_2SO_4 solution provided a potential interval for the passivation of the electrolyte/electrode system that was fully consistent with CV results. These potentials reflect the formation and subsequent preservation of a protecting ferric oxides layer, which enhances the resistance of the metal against the corrosive environment through the anodic protection imparted by the PAni EB Film, for a period of time determined. However, the film does not present good barrier properties. On the other hand, a commercial nitrocellulose paint was transformed into a passivating coating for steel in H_2SO_4 by adding a small amount (*i.e.* 0.25% - 0.50%) of the formulated PAni EB binder.

On the other hand, after the effective anodic protection period, coatings developed in this work (PAni EB Film and Smart Paint) did not undergo a re-oxidation, even though they were maintained in an oxygen-containing environment. Such re-oxidation is essential to enlarge the protection imparted to the coated metal against the corrosion.

5. ACKNOWLEDGEMENTS

Financial support from CNPq (135245/2009-5 process), CAPES (BEX 5413/10-9 and CAPES/DGU 157/08), MICINN and FEDER (MAT2012-34498) and Generalitat de Catalunya (research group 2009 SGR-925) is gratefully acknowledged. Support for the research of C.A. was received through the prize ‘‘ICREA Academia’’ for excellence in research funded by the Generalitat de Catalunya.

6. LIST OF REFERENCES

[1] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon, New York, 1966.

[2] M.A. Edeleanu, Corrosion Control by Anodic Protection, Platinum Metals Rev. 4 (1960)86-91.

[3] P. Novák, Anodic Protection. (Chapter 4.24) in Shreir´s Corrosion, Elsevier Science, Amsterdam, p 2857-2889, 2010.

[4] L.L. Shreir, R.A. Jarman, G. T. Burstein, Corrosion, ed. Third, v. 2, Elsevier, 2003.

[5] J.I. Munro, W.W. Shim, Anodic protection-its operation and applications, Mater. Performance**.** 5 (2001) 22-25.

[6] M.C. Deyá, B. del Amo, E. Spinelli, R. Romagnolli, The assessment of a smart anticorrosive coating by the electrochemical noise technique, Prog. Org. Coat. 76 (2013) 525-532.

[7] N. Selvakumar, K. Jeyasubramanian, R. Sharmila, Smart coating for corrosion protection by adopting nano particles, Prog. Org. Coat. 74 (2012) 461-469.

[8] M.J. Palimi, M. Rostami, M. Mahdavian, B. Ramezanzadeh, Aplication of EIS and salt spray tests for investigation of the anticorrosion properties of polyurethane-based nanocomposites containing Cr2O3 nanoparticles modified with 3-amino propyl trimethoxy silane, Prog. Org. Coat. Available online 23 July 2014.

[9] D.W. DeBerry, Modification of the Electrochemical and Corrosion Behavior of Stainless Steels with an Electroactive Coating, J. Electrochem. Soc. 132 (1985) 1022-1026.

[10] M.C. Bernard, A. Hugot-LeGoff, S. Joiret, Polyaniline layer for Iron Protection in sulfate medium, Synth. Met. 102 (1999) 1383-1384.

[11] N. Ahmad, A.G. MacDiarmid, Inhibition of corrosion of steels with the exploitation of conducting polymers, Synth. Met. 78 (1996) 103-110.

[12] A. Meneguzzi, M.C. Pham, J.C. Lacroix, B. Piro, A. Adenier, C.A. Ferreira, P.C. Lacaze, Electroactive Poly(Aromatic Amine) Films for Iron Protection in Sulfate Medium. P. C. J. Electrochem. Soc. 148 (2001) 121-126.

[13] E.T. Kang, K.G. Neoh, D.L. Tan, Polyaniline: a polymer with many Interesting intrinsic redox states, J. Prog. Polym. Sci., 23, (1998) 211-324.

[14] S. Sathiyanarayanan, K. Balakrishanan, S.K. Dhawan, D.C. Trivedi, Prevention of corrosion of iron in acidic media using poly(o-methoxy-aniline). Electrochimica Acta. 6 (1994) 831-837.

[15] B.Wessling, J. Posdorfer, Corrosion prevention with an organic metal (polyaniline): corrosion test results. Electrochimica Acta. 12 (1999) 2139-2147.

[16] W. Lu, R.L. Elsenbaumer, B. Wessling, Corrosion protection of mild steel by coatings containing polyaniline. Synth. Met. 71 (1995) 2163-2166.

[17] D.E. Tallman, G. Spinks, A. Dominis, G.G. Wallace, Electroactive conducting polymers for corrosion control part 1: general introduction and a review of nonferrous metals. J. Solid State Electrochem. 6 (2002)73-84.

[18] G.M. Spinks, A.J. Dominis, G.G. Wallace, D.E. Tallman, Electroactive conducting polymers for corrosion control part 2: ferrous metals. J. Solid State Electrochem. 6 (2002) 85-100.

[19] E. Armelin, C. Alemán, J. I. Iribarren, Anticorrosion performances of epoxy coatings modified with polyaniline: A comparison between the emeraldine base and salt forms. Prog. Org. Coat. 65 (2009) 88-93.

[20] T.A. Skotheim, J.R. Reynolds, "Handbook of conducting Polymers. Conjugated polymers: theory, synthesis, properties and characterization", Taylor-Francis, New York 2007.

[21] K.K.S. Kumar, S. Geetha, D.C. Trivedi, Freestanding conducting polyaniline film for the control of electromagnetic radiations, Curr. Appl. Phys. 5 (2005) 603-608,.

[22] E. Akbarinezhad, M. Ebrahimi, H.R. Faridi, Corrosion inhibition of steel in sodium chloride solution by undoped polyaniline epoxy blend coating, Prog. Org. Coat. 64 (2009) 361-364.

[23] D.P. Silva, R. Neves, A.J. Motheo, Electrochemical Behaviour of the AA2024 Aluminium Alloy Modified with Self-Assembled Monolayers/Polyaniline Double Films. Mol. Cryst. Liq. Cryst. 521 (2010) 179-186.

[24] E.M.; Geniès, A. Boyle, M. Lapkowski, C. Tsintavis, Polyaniline: A historical survey, Synth. Met. 36 (1990) 139-182.

[25] C. Alemán, C.A. Ferreira, J. Torras, A. Meneguzzi, M. Canales, M. A. S. Rodrigues, J. Casanovas, On the molecular properties of polyaniline: A comprehensive theoretical study, Polymer. 49 (2008) 5169-5176.

[26] E. Erdem, M. Karakisla, M. Saçak, The chemical synthesis of conductive polyaniline doped with dicarboxylic acids, Eur Polym J. 40 (2004) 785-791.

[27] A.F. Baldissera, C.A. Ferreira, Coatings basead on electronic conducting polymers for corrosion protection of metals, Prog. Org. Coat. 75 (2012) 241-247.

[28] T.Siva, K. Kamaraj, S. Sathiyanarayanan, Epoxy curing polyaniline (PANI) – Characterization and self-healing evaluation, Prog. Org. Coat. 77 (2014) 1095-1103.

[29] A. Kalendová, D. Veselý, M. Kohl, J. Stejskal, Effect of surface treatment of pigment particicles with polypyrrole and polyaniline phosphate on their corrosion inhibiting properties in organic coatings. Prog. Org. Coat. 77 (2014) 1465-1483.

[30] J. Stejskal, R.G. Gilbert, Polyaniline. Preparation of a Conducting Polymer, Pure Appl. Chem. 74 (2002) 857–867.

[31] M. Saçak, U. Akbulut, D. N. Batchelder, Characterization of electrochemically produced, two-component films of conducting polymers by Raman microscopy. Polymer. 39 (1998) 4735 -4739.

[32] I. Sedenkova, M. Trchova, J. Stejskal, Thermal degradation of polyaniline films prepared in solutions of strong and weak acids and in water – FTIR and Raman spectroscopic studies. Polymer Degrad. and Stab. 93 (2008) 2147-2157.

[33] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. John-Wiley: New Jersey, 2009.

[34] C.M.S. Izumi, V.R.L. Constantino, A.M.C. Ferreira, M.L.A. Temperini, Spectroscopic characterization of polyaniline doped with transition metal salts, Synth. Met. 156 (2006) 654–663.

[35] J. Zhang, C. Liu, G. Shi, Raman Spectroscopic Study on the Structural Changes of Polyaniline During Heating and Cooling Processes, Appl. Pol. Sci., Vol. 96, p. 732–739, 2005.

[36] B. Wessling, S. Schröder, S. Gleeson, H. Merkle, S. Schröder, F. Baron, Reaction scheme for the passivation of metals by polyaniline, Mat. and Cor. 47 (1996) 439-445.

[37] G.M. Spinks, A.J. Dominis, G.G. Wallace, D.E. Tallman, Electroactive conducting polymers for corrosion control, Part 2. Ferrous metals, J. Solid State Electrochem., 6 (2002) 85-100.

[38] T. Skotheim, R. Elsenbaumer, J. Reynolds, Handbook of conducting polymers, ed. Second, Marcel Dekker, New York, 1998.

[39] A. Döner, R. Solmaz, M. Özcan, G. Kardas, Experimental and theoretical studies of thiazoles as corrosion inhibitors for mild steel in sulphuric acid solution, Corrosion Scien. 53 (2011) 2902–2913.

[40] G.S. Popkirov, E. Barsoukov, R.N. Schindler, Investigation of conducting polymer electrodes by impedance spectroscopy during electropolymerization under galvanostatic conditions, J. Electroanal. Chem. 425 (1997) 209-216.

[41] K. Roûberg, L. Dunsch, Electrochemical impedance spectroscopy on conducting polymer membranas, Electrochim. Ac. 44 (1999) 2061-2071.

[42] A.S. Sarac, M. Ates, B. Kilic, Electrochemical Impedance Spectroscopic Study of Polyaniline on Platinum, Glassy Carbon and Carbon Fiber Microelectrodes, Int. J. Electrochem. Sci., 3 (2008) 777 – 786.

[43] V. Horvat-Radoševic´, K. Kvastek, Three-electrode cell set-up electrical equivalent circuit applied to impedance analysis of thin polyaniline film modified electrodes, J. Electroanal. Chem. 631 (2009) 10–21.

[44] T.B. Hunter, P.S. Tyler, W.H. Smyrl, H. White, "Impedance Analysis of Poly(Vinylferrocene) Films, The Dependence of Diffusional Charge Transport and Exchange Current Density on Polymer Oxidation State", J. Electrochem. Soc., 134-9 (1987) 2198-2204.